THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

I. Studies on the Configuration of Cadmium, Zinc, and Platinum in Complex Ammines

II. Configurational Changes in Some Reactions of Complex Cobalt Compounds

III. Preparation and Properties of Complex Cobalt Compounds Containing 2,3-Butylenediamine

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LEALLYN BURR CLAPP

B.Ed., Eastern Illinois State Teachers College, 1935
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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1941

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THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

I. Studies on the Configuration of Cadmium, Zinc, and Platinum in Complex Ammines

Although the absolute configurations of a pair of optical isomers are not known for any compound at the present time, the relative space positions of some compounds may be found if the configuration of a given compound is designated. It has been possible, for example, to relate the configurations of the octahedral complex triethylenediamine compounds of cobalt, rhodium[4], and chromium[6]. If the optical isomer of triethylenediamine cobaltic chloride which gives a *dextro* rotation to plane polarized light at the sodium D line be designated as having the D configuration, the corresponding chromium complex with a *dextro* rotation also has the D configuration. On the other hand, the triethylenediamine rhodium chloride having a *dextro* rotation has the L configuration. These space relationships were found by two independent means: (1) Delepine's[3] "active racemate" method and (2) Werner's solubility rule. It was thought that tri-diamines of cadmium, zinc, and platinum might be used in the same ways to relate the generic configurations of these metal ammines.

Relating generic configurations by the "active racemate" method depends upon obtaining isomorphous compounds. An equimolecular mixture of two optical isomers such as *d*-K_3 [Co Ox_3] and *l*-K_3 [Co Ox_3] results in an inactive racemic compound. If, however, *d*-K_3 [Co Ox_3] is replaced by *d*-K_3 [Cr Ox_3], with which it is isomorphous, an active racemate is formed since the two optical isomers do not have equal though they do have opposite signs of rotation. To relate the configurations of platinum, cadmium, and zinc in tri-diamines, the following complexes were selected as possible isomorphous compounds: [Cd l-pn_3] $(NO_3)_2$, [Zn l-pn_3] $(NO_3)_2$, [Pt l-pn_3] $(CO_3)_2$, and their respective optical antipodes. The first two

are isomorphous as is shown by analysis of x-ray goniometer patterns of single crystals. It was not possible to relate the configuration of the platinum complex to the other two since single crystals of the carbonate could not be isolated.

Werner[9] made the assumption that two optically active compounds have the same generic configuration when the diastereoisomers formed with the same resolving agent are the less soluble ones. Application of this solubility rule to the triethylenediamine compounds of cadmium, zinc, and platinum with sodium *dextro*-camphornitronate as the resolving agent shows that the following ions have the same generic configuration: *d*-$[Cd\ en_3]^{++}$, *d*-$[Zn\ en_3]^{++}$, and *l*-$[Pt\ en_3]^{++++}$.

The last ion was isolated as the chloride but the first two could not be. Although a resolution of $[Zn\ en_3]\ Cl_2$ and $[Cd\ en_3]\ Cl_2$ has been reported[8] using sodium *dextro*-camphornitronate, it is shown that alcoholic hydrogen chloride completely decomposes the less soluble *dextro* diastereoisomers into the metal chlorides and three molecules of ethylenediamine hydrochloride.

Rotatory dispersion curve data indicate that $[Cd\ 1\text{-}pn_3]^{++}$, $[Zn\ 1\text{-}pn_3]^{++}$, $[Pt\ d\text{-}pn_3]^{++++}$, and *l*-$[Pt\ en_3]^{++++}$ all have the same generic configurations.

II. Configurational Changes in Some Reactions of Complex Cobalt Compounds

Configurational changes were studied in some cobalt complexes in the hope that a Walden inversion might be demonstrated. Changes of configuration in inversions now known in inorganic hexacovalent complexes occur when two atoms of anionic character are replaced by a bivalent negative group. Whether this condition is necessary for an inversion is still an unanswered question but no evidence was found to the contrary. No changes in the sign of rotation have been observed in reactions of *d*-$[Co\ en_2\ (NH_3)\ Cl]\ Cl_2$ with the hydroxides and carbonates of silver and potassium nor with the action of chlorinating agents (aqueous and alcoholic hydrogen chlor-

ide and thionyl chloride) on the optically active hydroxo ammino and aquo ammino compounds.

The same series of reactions was carried out with [Co 1-pn_2 (NH_3) Cl] Cl_2. In this case the hoped-for change in configuration was *trans* to *cis* but again none was observed. Dispersion curves of all the products and starting material show *trans* characteristics. That is, the curves are regular with no pronounced maxima or minima.

Reactions of *cis* and *trans* [Co en_2 Cl_2]Cl with a series of aliphatic and aromatic primary amines were carried out to see if any of the amines would react with *l*-[Co en_2Cl_2]Cl to form an optically active compound. The reactions, some of which have been run by Meisenheimer and Kiderlen[7] and by Ablov[1], are hastened considerably by grinding the reactants and solvent together in a mortar. By this method using *p*-toluidine, dextro chloro *p*-toluidine diethylenediamine cobaltic chloride is obtained at room temperature. With methyl and ethyl amines at 0°C the reaction takes a different course. A mixture of optically inactive [Co en_2 (OH) Cl] Cl and *d*-[Co en_2 RNH_2 (OH)] Cl_2 is obtained in these two cases. Evidence for the mechanism of formation of the optically active compound is given. The chloro amine complex is first formed when the nitrogen in the amine acts as a donor atom. The second chlorine atom is replaced when the amine acts as a base.

Ablov's contention that the basicity of amines and their action on *trans* [Co en_2 Cl_2] Cl are independent is strengthened by the fact that a variety of products is obtained from the green salt with aliphatic amines of the same basicity.

Twelve new compounds prepared in the course of this research are described.

III. Preparation and Properties of Complex Cobalt Compounds Containing 2,3-Butylenediamine

The preparation, properties, and reactions of complex cobalt compounds containing ethylenediamine and propylenediamine have been extensively studied but only three complex

compounds of cobalt containing 2,3-butylenediamine are reported[5] in the literature. Seven new compounds containing this diamine were prepared by methods adapted from those used in preparing corresponding ethylenediamine compounds. A qualitative comparison is made of the solubilities of some of these compounds and the corresponding ethylenediamine and propylenediamine compounds. Except in the *trans* dichloro complex, they are more soluble than the ethylenediamine and less soluble than the propylenediamine series. Compounds containing *meso*-butylenediamine are more soluble than those containing a mixture of *meso*- and *racemic*-butylenediamine.

An unsuccessful attempt was made to demonstrate a Walden inversion in the reaction of [Co d-bn_2 Cl_2] Cl with silver carbonate by grinding them together dry in one case and with an aged solution of the complex in the other. No change in configuration (indicated in dispersion curves) occurred, possibly due to the rapid aquation of the dichloro compound which would mean that the silver carbonate reacts with the same compound in both instances.

A resolution of *cis* [Co bn_2 Cl_2] Cl has been effected using ammonium *dextro*- alpha-bromcamphor-pi-sulfonate.

Chappell's[2] method of preparing 2,3 butylenediamine by reduction of dimethylglyoxime in alcoholic hydrogen chloride with a platinum oxide catalyst has been adapted to the Parr low-pressure hydrogenation apparatus. An improved method of separating *meso*- and *racemic*- butylenediamine using the hydrochlorides is described.

Bibliography

1. Ablov, Bull. soc. chim., [5], **3**, 2270 (1936).
2. Chappell, Thesis No. 333, Iowa State College (1935). Abstract; Iowa State Coll. J. Sci. **11**, 45 (1936).
3. Delepine, Bull. soc. chim., [5], **1**, 1256 (1934).
4. Delepine and Charonnat, Bull. soc. franc. mineral., **53**, 73 (1930).
5. Frejka and Zahlova, Collection Czechoslov. Chem. Comm., **2**, 639 (1930).
6. Jaeger, Bull soc. chim., [5], **4**, 1212 (1937).
7. Meisenheimer and Kiderlen, Ann., **438**, 238 (1924).
8. Neogi and Mukherjee, J. Indian Chem. Soc., **11**, 225 (1934).
9. Werner, Ber., **45**, 121 (1912).

VITA

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